

(19)



Europäisches Patentamt

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(11)

EP 0 853 091 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

15.07.1998 Bulletin 1998/29

(51) Int. Cl.⁶: C08F 10/00

(21) Application number: 97430001.4

(22) Date of filing: 13.01.1997

(84) Designated Contracting States:

FR

Designated Extension States:

AL LT LV RO SI

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(54) Polymerisation process

(57) The polymerisation of olefins in the gas phase carried out in the presence of a catalyst system comprising (a) a metallocene and (b) an activator is improved by the addition of a lower alkane to the reaction. The preferred alkane is pentane and is preferably added to the reactor as a liquid.

The activity of the catalyst system may be improved by the addition of the alkane.

Description

The present invention relates to a polymerisation process in particular to a gas phase polymerisation process using a catalyst system comprising an activated metallocene complex.

5 Catalysts based on metallocene complexes have been widely used for the polymerisation of olefins. These complexes are used in catalyst systems comprising a bis(cyclopentadienyl) transition metal as the complex and a cocatalyst. Such bis (Cp) transition metal complexes are referred to as metallocenes and are typically based on titanium or zirconium metals and when used are cocatalysed with aluminium compounds such as aluminoxanes. When used in 10 gas phase processes such bis (Cp) metallocene systems may be supported on silica.

More recently another type of transition metal complex has been used to prepare olefin polymers. Such complexes have a single cyclopentadienyl ring ligand and a hetero atom bonded to the metal atom and may also be used in conjunction with aluminoxanes. Such 'constrained geometry' catalysts are described in EP 420436 and EP 416815.

Similar catalyst systems are taught in EP 418044 and WO 92/00333. In these systems the catalyst is prepared as 15 the product of a mono(cyclopentadienyl) heteroatom metal complex and an ionic activator compound and such systems have been referred to as ionic mono(cyclopentadienyl) catalysts. Typical ionic activators for such systems may be exemplified by borates or boranes.

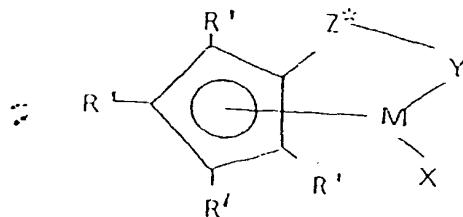
WO 95/00526 describes titanium or zirconium complexes in which the transition metal is in the +2 formal oxidation state. The complex also comprises a neutral, conjugated or non-conjugated diene ligand which forms a π -complex with 20 the metal. Such complexes are rendered catalysts by combination with an activating cocatalyst for example aluminoxanes, boranes or borates. When used in a gas phase polymerisation process such catalysts are also suitably supported on silica.

A particularly suitable process for polymerising olefins in the gas phase comprises a fluidised bed of growing polymer particles supported above a fluidisation grid. The bed is maintained in a fluidised state by the use of a fluidising medium which comprises a recycled gas stream which passes upwards through the fluidisation grid. In the fluidised bed 25 monomers and comonomers react together in the presence of a catalyst system.

We have now found that in such gas phase processes using activated metallocene catalyst systems an improvement in catalytic activity may be obtained by the injection of an inert liquid directly into the reactor.

Thus according to the present invention there is provided a process for the polymerisation of olefins in the gas phase said process being carried out in the presence of a catalyst system comprising (a) a metallocene and (b) an activator characterised in that a lower alkane is added directly to the gas phase reactor.

Titanium (II) or zirconium (II) complexes are particularly suitable for use in the process of the present invention. Such complexes are disclosed in the aforementioned WO 95/00526 which is incorporated herein by reference. The complexes have the general formula:-



wherein:

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof said R' having up to 20 non hydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral η^4 -bonded diene group having up to 30 non-hydrogen atoms, which forms a π -complex with M;

Y is -O-, -S-, -NR⁺-, -PH⁺;

M is titanium or zirconium in the +2 formal oxidation state;

Z* is SiR₂, CR₂, SiR^{*}₂SiR^{*}₂, CR^{*}₂CR^{*}₂, CR^{*} = CR⁺, CR₂SiR^{*}₂, or GeR^{*}₂; wherein:

R^{*} each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R^{*} having up to 10 non-hydrogen atoms, and optionally, two R^{*} groups from Z* (when R^{*} is not hydrogen), or an R^{*} group from Z* and an R^{*} group from Y form a ring system.

Most preferred complexes are amidosilane or amidoalkanediyl complexes wherein the metal is titanium.

Highly preferred diene groups are 1,4-diphenyl-1,3-butadiene, 1,3-pentadiene, 1,4-dibenzyl-1,3-butadiene, 3-methyl-1,3-pentadiene.

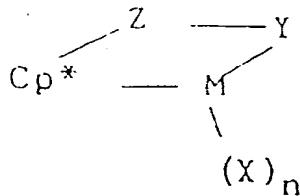
Illustrative but not limiting examples of complexes preferred are (tert-butylamido) (tetramethyl- η 5-cyclopentadienyl) dimethylsilane titanium (II) 1,4-diphenyl-1,3-butadiene,

(tert-butylamido) (tetramethyl- η 5-cyclopentadienyl) dimethyl silane titanium (II) 1,3-pentadiene,
(tert-butylamido) (2-methylindenyl) dimethylsilanetitanium (II) 1,4-diphenyl-1,3-butadiene.

These complexes are rendered catalytically active by combination with an activating cocatalyst. Suitable cocatalysts include aluminoxanes, especially methylaluminoxane (MAO) or strong Lewis acids eg tri (hydrocarbyl) boron compounds or halogenated derivatives.

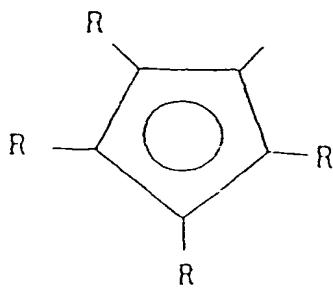
A particularly preferred activator is tris (pentafluorophenyl) boron.

Other complexes suitable for use in the process of the present invention are those in which the metal is in a higher valency state. Such complexes are disclosed in EP 416815 and WO 91/04257 both of which are incorporated herein by reference. The complexes have the general formula:



wherein:

30 Cp* is a single η 5-cyclopentadienyl or η 5-substituted cyclopentadienyl group optionally covalently bonded to M through -Z-Y- and corresponding to the formula:



45 wherein R each occurrence is hydrogen or a moiety selected from halogen, alkyl, aryl, haloalkyl, alkoxy, aryloxy, silyl groups, and combinations thereof of up to 20 non-hydrogen atoms, or two or more R groups together form a fused ring system;

50 M is zirconium, titanium or hafnium bound in an η 5 bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group and is in a valency state of +3 or +4.

X each occurrence is hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof (e.g. haloalkyl, haloaryl, halosilyl, alkaryl, aralkyl, silylalkyl, aryloxyaryl, and alkyoxyalkyl, amidoalkyl, amidoaryl) having up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms;

55 n is 1 or 2 depending on the valence of M;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;

Y is a linking group covalently bonded to the metal comprising nitrogen, phosphorus, oxygen or sulfur, or optionally Z and Y together form a fused ring system.

Most preferred complexes are those wherein Y is a nitrogen or phosphorus containing group corresponding to the formula (-NR¹) or (-PR¹) wherein R¹ is C₁-C₁₀ alkyl or C₆-C₁₀ aryl and wherein Z is SiR^{"2}, CR^{"2}, SiR^{"2}SiR^{"2}, CR^{"=CR"} or GeR^{"2} in which R" is hydrogen or hydrocarbyl.

5 Most preferred complexes are those wherein M is titanium or zirconium.

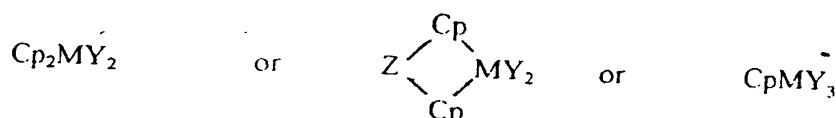
Illustrative, but not limiting examples of suitable complexes are (tert-butylamido) (tetramethyl- η^5 -cyclopentadienyl) dimethyl silanetitanium dimethyl, (tert-butylamido) dibenzyl (tetramethyl- η^5 -cyclopentadienyl) silane zirconium dibenzyl, (benzylamido) dimethyl (tetramethyl- η^5 -cyclopentadienyl) silane titanium dichloride, (phenylphosphido) dimethyl (tetramethyl- η^5 -cyclopentadienyl) silane zirconium dibenzyl and the like.

10 These complexes are rendered catalytically active by combination with an activating cocatalyst. Suitable cocatalysts include aluminoxanes, especially methylaluminoxane (MAO) or strong Lewis acids eg tri(hydrocarbyl) boron compounds or halogenated derivatives.

Particularly suitable as an activator is tris(pentafluorophenyl) boron.

Also suitable for use in the process according to the present invention are metallocene complexes having the general formula:

15



20

wherein

25 M is Zr, Ti or Hf
Y is a univalent ligand

Cp is an unsubstituted or substituted cyclopentadienyl ligand, and
Z is a bridging group

30 Typically the X group is halogen or alkyl and the cyclopentadienyl ligand may be substituted by alkyl groups or two substituents may be joined to form a fused ring eg indenyl.

Z is typically alkylene, dialkylsilyl or dialkylgermyl bridging group.

Particularly suitable complexes are for example ethylene bis(indenyl) zirconium dichloride or ethylene bis(indenyl) zirconium dimethyl.

35 Such metallocene complexes are typically used in the presence of aluminoxane cocatalysts.
Examples of such metallocene complexes suitable for use in the process of the present invention are those disclosed in EP 129368, EP 206794 and EP 260130.

Such bis(Cp) metallocene complexes may also be suitable for use in the process of the present invention when they process diene ligands. Complexes of this type are described in WO 96/04290.

40 The molar ratio of complex to activator employed in the process of the present invention may be in the range 1:10000 to 100:1. A preferred range is from 1:5000 to 10:1 and is most preferred in the range 1:10 to 1:1.

The alkane may be chosen from the group consisting of butane, pentane, isopentane or hexane. Preferably the alkane is pentane.

The pentane is most preferably added to the gas phase reactor before addition of the monomer or monomers. Preferably it is added as a liquid at room temperature.

45 The complexes according to the process of the present invention for use in the gas phase are supported.

Typically the support can be any organic or inorganic inert solid, particularly porous supports such as talc, inorganic oxides and resinous support materials such as polyolefins. Suitable inorganic oxide materials which may be used include Group 2, 13, 14 or 15 metal oxides such as silica, alumina, silica-alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania or zirconia. Other suitable support materials may be employed such as finely divided polyolefins such as polyethylene.

The most preferred support material for use with the supported catalysts according to the process of the present invention is silica.

It is preferable that the silica is dried before use and this is typically carried out by heating at elevated temperatures for example between 200 and 850 deg.C.

In a preferred protocol the supported catalyst may be prepared by addition of a solution of the activator in a suitable solvent to a slurry of activated silica treated with a trialkylaluminium compound followed by addition of a solution of the metallocene complex in the same solvent. Alternatively the complex may be added to the trialkylaluminium treated silica

before addition of the activator.

A suitable solvent for the preparation of the supported catalyst is toluene.

Suitable trialkylaluminium compounds are trimethylaluminium (TMA), triethylaluminium(TEA) or triisobutylaluminium (TIBAL).

The process according to the present invention is suitable for use in the polymerisation of olefins in particularly in the homopolymerisation of ethylene or the copolymerisation of ethylene with other alpha-olefins in particular those having from 3 to 10 carbon atoms. Most preferred alpha-olefins are 1-butene, 1-hexene and 4-methyl-1-pentene.

The process may be carried out in any suitable gas phase process but is particularly suitable for use with gas phase processes carried out in a fluidised bed reactor. A most preferred process is that described in WO 94/28032. Other suitable gas phase processes are described in EP 89691, WO 94/25495 and WO 94/25497.

The aforementioned WO 94/28032 relates to a fluidised bed gas phase process in which a liquid is injected directly into the fluidised bed. The liquid which may be an inert liquid is used as a condensate in order to aid the cooling of the bed. In such a process the liquid coolant may be continuously injected into the bed during the polymerisation process. In the present invention the alkane may be added to the reactor prior to the commencement of the polymerisation and is also used in much smaller amounts than used for cooling purposes as disclosed in WO 94/28032.

The alkane is particularly effective under polymerisation conditions of low comonomer concentrations. For example the invention is particularly suitable for the copolymerisation of ethylene and comonomer at pressures in the range $C_x/C_2 > 0.01$ bar preferably > 0.1 bar and C_x (absolute) > 0.1 bar preferably > 0.5 bar wherein C_x and C_2 are the partial pressures of comonomer and ethylene respectively.

Using the process according to the present invention polymers may be prepared having densities in the range from 0.905 to 0.960 g/cc and a melt index in the range 0.1 to 20 according to ASTM D1238 condition E (2.16 kg. at 190 deg.C).

The present invention will be further illustrated with reference to the following Examples.

Example 1

Preparation of supported catalyst 1

7.0kg of Crosfield ES70 silica (activated at 500°C) were slurried in 110 litres of hexane. 9.32 litres of 0.976M TEA in hexane were added, and the slurry agitated for 2 hours at 30°C. The silica was allowed to settle, and the supernatant hexane removed. The silica was washed several times with hexane, until the concentration of Al in the washing had reached <1mmol Al/litre. Then the silica was dried *in vacuo* at 40°C.

50g of this TEA treated ES70 silica were slurried in 250ml of dry toluene. 10.4ml of a 10.7wt% solution of (tert-butyliamido)(tetramethyl- n^5 -cyclopentadienyl)dimethylsilanetitanium penta-1,3-diene in toluene were added, and the mixture shaken vigorously. Then 29.4 ml of a 7.85wt% solution of tris(pentafluorophenyl)boron in toluene were added. The mixture was shaken well, and then the solvent removed *in vacuo* at 40°C to give an olive green powder.

Example 2

Preparation of supported catalyst 2

2.5kg of Crosfield ES70 silica (activated at 500°C) were slurried in 110 litres of hexane. 4.00 litres of 0.976M TEA in hexane were added, and the slurry agitated for 2 hours at 30°C. The silica was allowed to settle and the supernatant hexane removed. The silica was washed several times with hexane, until the concentration of Al in the washing had reached <1mmol Al/litre. Then the silica was dried *in vacuo* at 40°C.

10g of this TEA treated ES70 silica were slurried in 40ml of dry toluene 2.1ml of a 10.7wt% solution of (tert-butyliamido)(tetramethyl- n^5 -cyclopentadienyl)dimethylsilanetitanium penta-1,3-diene in toluene were added, and the mixture shaken vigorously. Then 5.9ml of a 7.85wt% solution of tris(pentafluorophenyl)boron in toluene were added. The mixture was shaken well, and then the solvent removed *in vacuo* at 40°C to give an olive green powder.

Example 3

Polymerisation.

347g of NaCl was added to a 2.5 litre volume agitated dry phase reactor, which had been previously baked out at 85°C under a N₂ purge. The reactor was cooled to 25°C and 5ml of dry pentane was added to the reactor. The reactor was sealed and the temp. raised to 85°C. 1.19g of a TIBAL treated silica was added to the reactor, and this was agitated for 15 minutes. The reactor was cooled to 70°C, and 6.5 bar C₂H₄ added. Then H₂ and 1-hexene were admitted to the

reactor. A mixture of 0.309g of catalyst prepared from example 1 and 0.912g of a TIBAL treated silica was injected into the reactor with high pressure N₂. The temperature, C₂H₄ pressure and H₂ and 1-hexane levels were maintained constant during the rest of the test. The total polymerisation time was 233 minutes. During the test, the average H₂/C₂H₄ ratio was 0.0038 and the average 1-hexene/C₂H₄ ratio was 0.0062. The reactor was vented and cooled, and 262g of 5 polymer was recovered after washing off the salt, giving an activity of 33.6g/g cat.h.bar. The polymer density was 0.9175 g/ml and M1(2.16) was 2.10.

Example 4

10 Polymerisation

289g of NaCl was added to a 2.5 litre volume agitated dry phase reactor, which had been previously baked out at 85°C under a N₂ purge. The reactor was cooled to 25°C and 5ml of dry pentane was added to the reactor. The reactor 10 was sealed and the temp. raised to 85°C. 1.30g of a TIBAL treated silica was added to the reactor, and this was agitated for 15 minutes. The reactor was cooled to 70°C, and 6.5 bar C₂H₄ added. Then H₂ and 1-hexene were admitted to the reactor. A mixture of 0.289g of catalyst prepared from example 1 and 0.853g of a TIBAL treated silica was injected into the reactor with high pressure N₂. The temperature, C₂H₄ pressure and H₂ and 1-hexene levels were maintained constant during the rest of the test. The total polymerisation time was 105 minutes. During the test, the average H₂/C₂H₄ 15 ratio was 0.0040 and the average 1-hexene/C₂H₄ ratio was 0.0060. The reactor was vented and cooled, and 144g of polymer was recovered after washing off the salt, giving an activity of 43.8g/g cat.h.bar. The polymer density was 0.9175 g/ml and M1(2.16) was 3.10. 20

Example 5

25 (Comparative)

344g of NaCl was added to a 2.5 litre volume agitated dry phase reactor, which had been previously baked out at 85°C under a N₂ purge. 1.30g of a TIBAL treated silica was added to the reactor, and this was agitated for 15 minutes. The reactor was cooled at 70°C, and 6.5 bar C₂H₄ added. Then H₂ and 1-hexene were admitted to the reactor. A mixture of 0.213g of catalyst prepared from Example 1 and 0.781g of a TIBAL treated silica was injected into the reactor with high pressure N₂. The temperature, C₂H₄ pressure and H₂ and 1-hexene levels were maintained constant during the rest of the test. The total polymerisation time was 166 minutes. During the test, the average H₂/C₂H₄ 30 ratio was 0.0039 and the average 1-hexene/C₂H₄ ratio was 0.0053. The reactor was vented and cooled, and 101g of polymer was recovered after washing on the salt, giving an activity of 26.3g/g cat.h.bar. 35

Example 6

Polymerisation

273g of NaCl was added to a 2.5 litre volume agitated dry phase reactor, which had been previously baked out at 40 85°C under a N₂ purge. The reactor was cooled to 25°C and 5ml of dry pentane was added to the reactor. The reactor was sealed and the temp. raised to 85°C. 1.21g of a TIBAL treated silica was added to the reactor, and this was agitated for 15 minutes. The reactor was cooled to 70°C, and 6.5 bar C₂H₄ added. Then H₂ and 1-hexene were admitted to the reactor. A mixture of 0.217g of catalyst prepared from Example 2 and 0.755g of a TIBAL treated silica was injected into the 45 reactor with high pressure N₂. The temperature, C₂H₄ pressure and H₂ and 1-hexene levels were maintained constant during the rest of the test. The total polymerisation time was 132 minutes. During the test, the average H₂/C₂H₄ ratio was 0.0042 and the average 1-hexene/C₂H₄ ratio was 0.0044. The reactor was vented and cooled, and 122g of polymer was recovered after washing off the salt, giving an activity of 39.3g/g cat.h.bar. The polymer density was 0.918 g/ml and M1(2.16) was 4.4. 50

Example 7

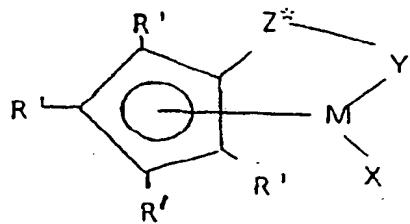
(Comparative)

322g of NaCl was added to a 2.5 litre volume agitated dry phase reactor, which had been previously baked out at 55 85°C under a N₂ purge. 1.19g of a TIBAL treated silica was added to the reactor, and this was agitated for 15 minutes. The reactor was cooled to 70°C, and 6.5 bar C₂H₄ added. Then H₂ and 1-hexene were admitted to the reactor. A mixture of 0.220g of catalyst prepared from example 2 and 0.754g of a TIBAL treated silica was injected into the reactor

with high pressure N₂. The temperature, C₂H₄ pressure and H₂ and 1-hexene levels were maintained constant during the rest of the test. The total polymerisation time was 123 minutes. During the test, the average H₂/C₂H₄ ratio was 0.0035 and the average 1-hexene/C₂H₄ ratio was 0.0037. The reactor was vented and cooled, and 85g of polymer was recovered after washing off the salt, giving an activity of 29.0g/g cat.h.bar. The polymer density was 0.919 g/ml and M1(2.16) was 0.8.

Claims

1. A process for the polymerisation of olefins in a gas phase reactor said process being carried out in the presence of a catalyst system comprising (a) a metallocene and (b) an activator characterised in that a lower alkane is added directly to the gas phase reactor.
2. A process according to claim 1 wherein the lower alkane is chosen from the group consisting of butane, pentane isopentane or hexane.
3. A process according to claim 2 wherein the alkane is pentane.
4. A process according to any of the preceding claims wherein the alkane is added directly to the reactor before the addition of the olefins.
5. A process according to any of the preceding claims wherein the alkane is added to the reactor as a liquid.
6. A process according to any of the preceding claims wherein the metallocene has the formula:



wherein:

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof said R' having up to 20 non hydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

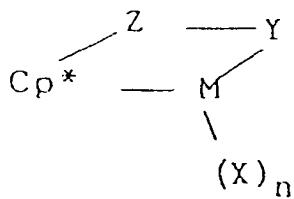
X is a neutral η^4 - bonded diene group having up to 30 non-hydrogen atoms, which forms a π -complex with M; Y is -O-, -S-, -NR⁺-, -PR⁺;

M is titanium or zirconium in the +2 formal oxidation state;

Z^{*} is SiR₂, CR^{*}₂, SiR^{*}₂SiR^{*}₂, CR^{*}₂CR^{*}₂, CR^{*} = CR^{*}, CR₂SiR^{*}₂, or GeR^{*}₂; wherein:

R^{*} each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R^{*} having up to 10 non-hydrogen atoms, and optionally, two R^{*} group from Z^{*} (when R^{*} is not hydrogen), or an R^{*} group from Z^{*} and an R^{*} group from Y form a ring systems.

7. A process according to any of the preceding claims wherein the metallocene has the formula:

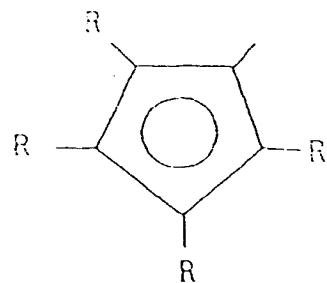


10

wherein:

15 Cp* is a single η^5 -cyclopentadienyl or η^5 -substituted cyclopentadienyl group optionally covalently bonded to M through -Z-Y- and corresponding to the formula:

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25

30 wherein R each occurrence is hydrogen or a moiety selected from halogen, alkyl, aryl, haloalkyl, alkoxy, aryloxy, silyl groups, and combinations thereof of up to 20 non-hydrogen atoms, or two or more R groups together form a fused ring system;

35 M is zirconium, titanium or hafnium bound in an η^5 bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group and is in a valency state of +3 or +4.

40 X each occurrence is hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof (e.g. haloalkyl, haloaryl, halosilyl, alkaryl, aralkyl, silylalkyl, aryloxyaryl, and alkyloxyalkyl, amidoalkyl, amidoaryl) having up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms;

45 n is 1 or 2 depending on the valence of M;

50 Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;

Y is a linking group covalently bonded to the metal comprising nitrogen, phosphorus, oxygen or sulfur, or optionally Z and Y together form a fused ring system.

8. A process according to any of the preceding claims wherein the metallocene is supported.

45 9. A process according to claim 8 wherein the metallocene is supported on silica.

10. A process according to any of the preceding claims wherein the polymerisation process is carried out in a fluidised bed reactor.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 43 0001

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X,D	WO 94 28032 A (BP CHEM INT LTD ;CHINH JEAN CLAUDE (FR); FILIPPELLI MICHEL CHARLES) 8 December 1994 * page 5, line 32 - page 7, line 10 * * page 8, line 2 - line 21 * ---	1-5,10 6-9	C08F10/00
A	WO 96 20780 A (BP CHEM INT LTD ;NEWTON DAVID (GB)) 11 July 1996 * page 9, line 11 - page 10, line 5 * ---	1-5,10 6-9	
X	US 5 462 999 A (GRIFFIN JOHN R ET AL) 31 October 1995 * column 5, line 50 - column 6, line 48 * * column 8, line 42 - column 9, line 7 * * column 19, line 53 - column 20, line 18 *	1-5,10 6-9	

			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08F
<p><i>NOTICE OF REJECTION OF CLAIMS</i></p>			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	13 June 1997	Schmidt, H	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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